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20 augustus 1969; Amerikaanse octrooiaanvraag 860.794
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17.893 van 9 maart 1970Korte aanduiding: "Werkwijze ter bereiding van een wasmiddelsamen-
stelling"

De uitvinding heeft betrekking op een werkwijze ter bereiding van een wasmiddelsamenstelling, in het bijzonder van een wasmiddelsamenstelling die bestemd is voor het wassen van weefsels, alsmede van builders die in dergelijke samenstellingen kunnen worden toegepast.

5 In wasmiddelsamenstellingen, in het bijzonder wanneer die bestemd zijn voor het wassen van weefsels, worden gewoonlijk synthetische, wasactieve verbindingen tezamen met builders opgenomen. De conventionele wasmiddelbuilders zijn gewoonlijk anorganische stoffen, in het bijzonder gecondenseerde fosfaten, zoals bijvoorbeeld natriumtripolyfosfaat. Men

10 heeft er echter op gewezen dat het gebruik van fosfaatbuilders kan bijdragen tot het optreden van eutropificatieproblemen. Andere organische

BAD ORIGINAL

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DETERGENT COMPOSITIONSPatent Number: ☐ GB1330121Publication
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Abstract

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(54) DETERGENT COMPOSITIONS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London, E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

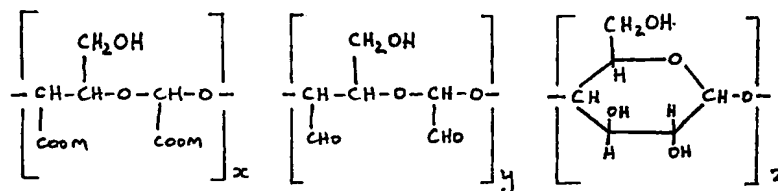
The invention relates to detergent compositions, and in particular to detergent compositions adapted for fabric washing and to detergency builders for use in such compositions.

Detergent compositions, particularly when adapted for fabric washing, commonly incorporate synthetic detergent active compounds together with detergency builders. Conventional detergency builders are commonly inorganic materials, particularly condensed phosphates such, for example as sodium tripolyphosphate. It has, however, been suggested that the use of phosphate detergency builders can contribute to eutrophication problems. Alternative organic detergency builders which have been suggested, for example sodium ethylene diamine tetraacetate (EDTA), sodium nitrilotriacetate (NTA) and synthetic polyelectrolyte materials, tend to be expensive and less efficient than the phosphate detergency builders, or otherwise unsatisfactory for one reason or another. For example, the synthetic polyelectrolyte builders proposed tend to be hygroscopic and largely non-biodegradable.

We have now found that water soluble or dispersible oxidised polysaccharides containing a proportion of dicarboxylic units, which are derived by oxidative cleavage of the original monosaccharide rings, can be used as detergency builders. For convenience such oxidised polysaccharides are termed dicarboxyl polysaccharides hereinafter.

The preferred detergency builders of the compositions of the invention can be generally represented by the following formula:

(1)



wherein M is a hydrogen atom, an alkali metal ion, or an ammonium, alkanolammonium, morpholinium or tetramethyl ammonium group; x is from 20% to 100%; y is from 0 to 80%, and z is from 0 to 80% per 100 original anhydroglucose units of the molecule. For

convenience, the basic molecular structures within the y and z brackets are referred to hereinafter as dialdehyde units and anhydroglucose units respectively, whilst the basic molecular structure within the x brackets is a type of dicarboxyl unit mentioned earlier.

Within the broad class of these preferred compounds, there are three distinctive types of dicarboxyl polysaccharide which can be classified by the amounts of the x, y and z units present in the final compound. For purposes of this invention, the different types are represented as follows:

Type I x is from 20% to 94%
 y is from 3% to 80%
 z is from 0 to 3%
 Type II x is from 20% to 100%
 y is 0
 z is from 0 to 80%

and Type III x is from 20% to 94%
 y + z is from 6% to 80%
 wherein the value of z is greater than 3% and y is greater than 0

It is to be understood that the references in the specification to the percentages of the dicarboxyl, dialdehyde and anhydroglucose units means the number of dicarboxyl, dialdehyde and anhydroglucose units per 100 original anhydroglucose units of the molecule.

The Type II dicarboxyl polysaccharide, in which there are no dialdehyde units present, has been suggested in the prior art as a soil suspending agent, in US Patent No. 2,894,945. In this case only minor amounts not exceeding 5% of the dicarboxyl polysaccharides would be used in detergent compositions. The use of the dicarboxyl polysaccharides as detergency builders in place of existing builders or to supplement such builders in a detergent composition has not been suggested hitherto.

Oxidation of the polysaccharides can be accomplished in two stages, in the first of which the monosaccharide rings are opened to give two aldehyde groups at the site of each ring cleavage, and in the second stage some or all of the aldehyde groups are oxidised to carboxylic acid groups. Alternatively, the reaction can be accomplished in a single step, depending on the oxidising agents used.

The accomplishment of the reaction in two separate stages is to be preferred if it is desired that the dicarboxyl polysaccharide should contain a proportion of dialdehyde units, as otherwise the tendency is for each ring opened to be oxidised to dicarboxyl units. The preferred oxidising agent which can be used to cleave the monosaccharide ring but not cause any substantial cleavage of the glycoside links between the monosaccharide units is periodic acid and its soluble salts. Other specific oxidising agents which may be mentioned are lead tetraacetate, sodium bismuthate and phenyl iodoso diacetate. Certain polysaccharides, particularly starch, which have been partly oxidised as described so as to contain a proportion of dialdehyde units are commercially available, for example as so-called dialdehyde starch.

In the second step, when the stages are kept separate, the aldehyde groups are oxidised further to the carboxylic acid groups. Examples of specific oxidising agents for the second step are lithium, sodium, potassium, caesium or rubidium chlorite, of which sodium and potassium chlorite are preferred for economic reasons. The salt used for the oxidising agent in the second step will contribute to the salt form of the dicarboxyl units. Thus, if sodium chlorite is used, the sodium salt form of the dicarboxyl unit will be present in the product. Alternatively, the alkali metal salt form can be ion-exchanged to produce the free acids which can then be neutralised with other alkali metal hydroxides, ammonium hydroxide or organic bases such as monoethanolamine, diethanolamine, triethanolamine, morpholine, and tetramethyl ammonium hydroxide. However, if a non-nitrogen, non-phosphate builder is desired, then only the alkali metal salts would be used. It is immaterial which salt form is present, since they all have similar detergency building characteristics.

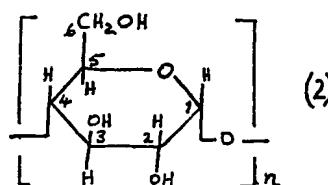
It is advantageous to accomplish the oxidation to form Type II dicarboxyl polysaccharides in a single step using only one oxidising agent. In this process, the polysaccharide is reacted directly with an alkali metal hypohalite, preferably sodium hypo-

chlorite, to produce the desired materials. In order to accomplish the oxidation with sodium hypochlorite so as to obtain the desired ring cleavage to give dicarboxyl polysaccharides with a minimum degree of side reactions, it is necessary to use alkaline conditions, preferably at pH 7.5 to pH 9. In particular it has been found that the use of a pH within the range of 8 to 8.5, preferably 8.25, gives optimum results in terms of the detergency building performance of the dicarboxyl polysaccharides. Attention is directed to the Applicant's copending patent application No. 6379/73 (Serial No. 1,330,123) which claims this process for oxidising polysaccharides.

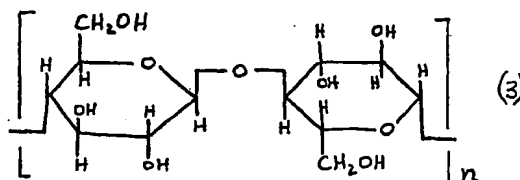
It will be appreciated that the two-stage oxidation process is much more expensive to use than the single stage oxidation with sodium hypochlorite. Periodic acid and its salts are the cheapest reagents for accomplishing the first oxidation stage, but even these are expensive. However, it is possible to decrease the cost of periodate oxidation by using an electrolytic regeneration process for periodate ions.

Any polysaccharide containing vicinal hydroxyl groups may be used as the starting material for forming the detergency builders of the invention, examples of which are starches such as corn, potato, rice, arrow root, tapioca, wheat and sago starches; dextrin; cellulose; glycogens; dextrans; sucrose; oligosaccharides; polyuronic acids such as pectin and alginic acid and natural gums such as agar, arabic, acacia, ghatti and karaya. It is also possible to use as starting materials polysaccharides which have been chemically modified, for example by partial hydrolysis, esterification, etherification, carboxylation or cross-linking prior to or during oxidation, provided they can still be oxidised to the dicarboxyl polysaccharides for use according to the invention. For reasons of availability and cost it is generally preferred to use either starch or cellulose (natural or regenerated).

It will be appreciated that only certain polysaccharides when oxidised give the preferred Type I, Type II or Type III materials. The polysaccharides which do so are those having six-membered monosaccharide rings with a 5-hydroxy methyl group, as in the case of starch and cellulose which have the nominal formulae: —



starch



cellulose

Whereas starch is an α -glucoside, cellulose is a β -glucoside and has a different form of linkage between the anhydroglucose rings. Both types of linkage are embraced in the general formula (1) shown earlier.

It should be understood that the dicarboxyl units of the oxidised polysaccharides may be in any order in the molecules, and in the case of the dicarboxyl polysaccharides with dialdehyde units, these may also be in random order. For example, in some molecules there may be many dicarboxyl units connected to each other before the appearance of a dialdehyde unit or units or an anhydroglucose unit or units. However, the distribution of the dicarboxyl and any other units in the dicarboxyl polysaccharides is not believed significantly to effect the detergency building properties of the materials.

Further, the molecular weight of the dicarboxyl polysaccharides will also vary, depending in particular on the molecular weight of the starting material. The molecular weight can also be changed by the method of oxidation used as some methods, particularly oxidation with sodium hypochlorite, tend to cause depolymerisation.

Also, it must be understood that the formula (1) is a very much simplified representation of the actual chemical structures involved. More specifically, it is well-known for example that many starches can contain as a major constituent thereof amylopectin which has a branched-chain structure as opposed to the linear chain molecule of α -amylose. Since the amylopectin polymers are linked by hemiacetal links at the uronic 6-hydroxyl position, derivatives such as the dicarboxyl starches may also contain considerable substitution at the uronic hydroxyl sites besides the simple linear chains described above. It is also apparent that the structural unit may contain mixed functional groups, as for example an aldehyde and a carboxyl group.

If cellulose is used as the starting material for making the detergency builder, the structure of the dicarboxyl polysaccharide is also complex. The repeating unit in cellulose is cellobiose, the number of which units, n in formula (3), is generally in the range of 250 to 2,500.

As in the case of starch, the dicarboxyl cellulose can be formed by first oxidising the cellulose to cleave the anhydro-glucose rings and thus produce the intermediate dialdehyde unit, and thereafter the material is further oxidised to produce the dicarboxyl units. Alternatively, the formation of dicarboxyl units can be completed in a single process. One or both rings of each cellobiose unit are capable of being cleaved resulting in a random distribution of the dicarboxyl units, dialdehyde units and anhydro-glucose units in the final dicarboxyl polysaccharide molecule. However, the material obtained can still be characterised by the formula (1); that is, the three monomer units are present in the stated percentages, although the sequence of the units in relationship to each other is unknown.

As explained above, there are three distinctive types of structures which are characterised by the proportions of the dicarboxyl units, the dialdehyde units and the anhydroglucose units present in the dicarboxyl polysaccharide molecules. While all three types of structures; that is, the Type I and Type III compounds formed from three monomer units and the Type II compounds formed from two monomer units, are excellent detergency builders in detergent compositions, it is found that it is easier to process the Type I and Type III compounds through standard process equipment, at savings of cost and equipment.

While it is not completely understood as to why the Type I and Type III dicarboxyl polysaccharides can be processed more readily than the Type II materials, it is presumably due to the presence of the dialdehyde units. More specifically, it is speculated that the dicarboxyl polysaccharides with dialdehyde units have a decreased affinity for water and hence decreased hygroscopic properties. Thus, when the compounds are used in powdered detergent formulations, processing is easier to control and the formulations have superior physical stability.

Further, it has also been found that because of the presence of greater amounts of the anhydroglucose units in the Type III dicarboxyl polysaccharides than found in the Type I materials, the Type III material is more readily biodegradable. Thus, this material is even more preferred, since it is more apt to degrade even under adverse biological conditions.

It will be appreciated that some of the polysaccharides such as alginic acid already contain carboxyl groups in which case these materials on oxidation to the dicarboxyl polysaccharides have some repeating units with three carboxyl groups. It is also possible to make similar materials, for example by oxidation of the hydroxyl methyl attached to the anhydroglucose ring preferably before the oxidative ring cleavage takes place. The product of such a process is a tricarboxyl polysaccharide, for example tricarboxyl starch.

It is essential to oxidise the polysaccharides to the extent of providing at least 20% (as herein defined) of dicarboxyl units in the product. This is the minimum level for any significant detergency building effect. However, at this level of oxidation the materials are hardly water-soluble, and it is generally desirable to oxidise the materials to open at least 50%, and preferably at least 60% of the anhydroglucose rings.

According to this invention, excellent cleaning results can be obtained by using the dicarboxyl polysaccharide detergency builders described above with a wide range of detergent active compounds or mixtures thereof. The dicarboxyl polysaccharides can be used alone, or in mixtures, or in combination with other detergency builders such as sodium nitrilotriacetate, sodium ethylene diamine tetraacetate, sodium alkenyl succinates, sodium tripolyphosphate, sodium and potassium pyrophosphates, polyelectrolyte builders such as sodium polyacrylate, sodium polymaleate and sodium copolyethylene maleate. It has been found that when the detergency builders of the present invention are used with other types of detergency builders, particularly alkali metal nitrilotriacetates, the detergency building properties are enhanced.

In the detergent compositions of the present invention the only essential ingredients are the detergent active compound and the dicarboxyl polysaccharide detergency builder. The amount of the detergency builder present in the detergent compositions is more than 5% by weight up to 90%, and preferably from 20% to 60% by weight, for example from 30 to 50% by weight, and the ratio by weight of the detergent active compound to the detergency builder is from 3:1 to 1:10.

The detergent active compounds which can be used in the compositions of this invention include anionic, nonionic, zwitterionic, ampholytic detergent compounds and mixtures thereof.

Suitable anionic detergent compositions which can be used include both soap and non-soap detergent compounds. Examples of suitable soaps are the sodium, potassium, ammonium and alkylolammonium salts of higher fatty acids ($C_{10}-C_{20}$). Particularly useful are the sodium or potassium salts of the mixtures of fatty acids derived from coconut oil and tallow. The usual synthetic anionic detergent active compounds are the water soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of such synthetic detergent active compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher (C_8-C_{18}) alcohols produced by reducing the glycerides of tallow or coconut oil; sodium and potassium alkyl (C_8-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl ($C_{10}-C_{16}$) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane sulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to cover the material made by reacting olefins, particularly alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product.

Examples of suitable nonionic detergent active compounds include the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6-C_{12}) phenols, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8-C_{18}) alcohols with ethylene oxide, generally 6 to 30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine.

Other suitable nonionic detergent active compounds include long chain tertiary amine oxides of the general formula, $R_1R_2R_3N \rightarrow O$, for example wherein R_1 is an alkyl (C_8-C_{18}) radical and R_2 and R_3 are each methyl, ethyl or hydroxy ethyl radicals; long chain tertiary phosphine oxides of the general formula $RR'R''P \rightarrow O$, for example wherein R is an alkyl, alkenyl or monohydroxyalkyl radical with C_{10} to C_{18} carbon chain length and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms; and dialkyl sulfoxides of the general formula, $RR'S \rightarrow O$, for example wherein R is an alkyl, alkenyl, beta- or gamma-monohydroxyalkyl radical or an alkyl or beta- or gamma-monohydroxyalkyl radical containing one or two other oxygen atoms in the chain, the group R having a 10 to 18 carbon chain length, and R' is a methyl, ethyl or alkylol group.

Suitable ampholytic synthetic detergents are derivatives of aliphatic secondary and tertiary amines, with at least one C_8 to C_{18} aliphatic radical and with an anionic water solubilising group, for example sodium N-2-hydroxyalkyl-N-methyl-taurates.

Suitable zwitterionic synthetic detergents are derivatives of aliphatic quaternary ammonium compounds, sulphonium compounds and phosphonium compounds with at least one C_8 to C_{18} aliphatic radical and an anionic water solubilising group, for example N-(C_8 — C_{18})alkyl-N,N-dimethylammoniopropane sulphonate.

In addition to the essential ingredients in the detergent composition, other optional ingredients may also be added, for example perfumes, colourants, fabric softening agents, fungicides, germicides, enzymes, fluorescent agents, anti-redeposition agents such as sodium carboxymethyl cellulose, hydrotropes and in the case of liquid compositions, opacifiers and organic solvents such as lower aliphatic alcohols. Other ingredients such as bleaches, for example sodium perborate with or without the presence of peracid precursors, active chlorine compounds and inorganic salts such as sodium carbonate, sodium sulphate, sodium chloride and sodium silicate may also be present if desired.

The compositions of the invention may be solid compositions, for example in powdered, granular or tablet form, semi-solid paste or gel compositions or they may be liquid compositions. Whilst the compositions are of particular utility in the field of fabric washing, they can also be used for general cleaning purposes and, if desired, for personal washing.

The production of dicarboxyl polysaccharides and their assessment for detergency building properties in relation to sodium tripolyphosphate, using either light reflectance measurements or a radio tracer method, are described in the following Examples, in which parts and percentages are by weight except where otherwise indicated.

Example 1.

60 g. of sodium metaperiodate was added to 1,250 ml of water and the pH of the resultant solution adjusted to pH 3.5 by addition of concentrated hydrochloric acid (3.8 ml). 40 g. of cellulose ("Rayweb Q") was added to the solution which was stirred for a period of 7 days in a darkened vessel at room temperature. After this period 78% of the sodium metaperiodate had been consumed and the dialdehyde cellulose was filtered off and washed with cold water to remove sodium iodate and sodium metaperiodate.

The dialdehyde cellulose was further oxidised using 72 g. of commercial sodium chlorite (80%) and 22.4 ml of glacial acetic acid in 640 ml of water. After a period of 2 hours the reaction mixture was purged with gaseous nitrogen to remove excess chlorine dioxide. The product was precipitated with 2.5 l of acetone and neutralised to pH 8.5 using N/10 NaOH and finally dialysed against distilled water for 8 hours. 39 g. of the dicarboxyl cellulose was recovered by reprecipitation using acetone, and was found to contain 75% dicarboxyl units.

Example 2.

The detergency building effect of the dicarboxyl cellulose of Example 1, in a detergent composition comprising 2 parts of the dicarboxyl cellulose to 1 part of sodium dodecyl benzene sulphonate as the detergent active compound, was determined by the preparation of an aqueous solution of the dicarboxyl cellulose (0.1%), sodium silicate ($SiO_2:Na_2O=2:1$) (0.025%) and the sodium dodecyl benzene sulphonate (0.05%) in water of 25° H (250 ppm Ca. hardness.) The solution (pH adjusted to 10) was heated to 45° C. and used to wash a cotton test cloth impregnated with a carbon-14 labelled synthetic sebum, the radioactive count of the cloth before and after washing being measured. The detergency, (the percentage change in radioactive count) of the dicarboxyl cellulose composition was 59%, whereas by way of comparison the detergency of a similar solution in which the dicarboxyl cellulose was replaced by sodium tripolyphosphate was 61.7%.

A sample of the dicarboxyl cellulose of Example 1 was exposed to an atmosphere of 90% relative humidity at 20° C. to test its hygroscopicity, when it was found to absorb an amount of water of the same order as that for sodium tripolyphosphate, but much less than that for synthetic polyelectrolyte detergency builders such as sodium polyacrylate.

Example 3.

17.2 g. of pure cellulose (Celufi; $H_2O=5.7\%$) was oxidised to dialdehyde cellulose using the same method and quantities described for making dialdehyde starch by Mehlretter in *Methods In Carbohydrate Chemistry*, edited by R. L. Whistler, Vol. IV p.316 (1964), Academic Press. The yield of dialdehyde cellulose was 14.9 g. dialdehyde units (dry basis) as determined by the method of Hofreiter et al in *Anal. Chem.* 27 1930 (1955).

13.30 g. of the above prepared dialdehyde cellulose was dispersed in a stirred solution of 40 mg of sodium carbonate in 400 ml of distilled water at about $88^\circ C$, stirred for 30 minutes to obtain a complete dispersion of the dialdehyde starch. After cooling the dispersion to room temperature, 90 ml of a freshly made solution containing 52 g. of sodium chlorite, 16 ml glacial acetic acid and distilled water was added slowly to the dispersion. An evolution of chlorine dioxide gas and a slight evolution of heat occurred. The reddish brown mixture was then stirred for 24 hours at room temperature. Nitrogen was then bubbled through the resulting yellow solution to remove chlorine dioxide.

The dicarboxyl cellulose was precipitated by pouring the reaction mixture, into 2 volumes of industrial alcohol. After decanting, the gummy white product was redissolved in a minimum amount of water and reprecipitated with industrial alcohol. This purification procedure was repeated until a test for Cl^- was negative. The product was then dried in a vacuum oven over P_2O_5 at $45^\circ C$. for 24 hours to give 18.0 g. of dicarboxyl cellulose ($H_2O=0.21\%$). It contained 92% dicarboxyl units (dry basis), as determined by the ion-exchange method of Hofreiter et al (*JACS* 79, 6457 (1957) 7% dialdehyde units and 1% anhydroglucose units by difference from the composition of the starting dialdehyde cellulose.

Examples 4 and 5.

A detergent composition was prepared using the dicarboxyl cellulose of Example 3 as detergency builder, and a further composition was made for comparative purposes using sodium tripolyphosphate. The compositions were then tested for detergency or cleansing ability in the Terg-O-Tometer Test using a 65% "Dacron"* polyester 35% cotton test cloth soiled with vacuum cleaner dust. The washing was conducted in water of $120^\circ F$. ($50^\circ C$.) and 180 ppm hardness ($2/1 Ca^{++}/Mg^{++}$) using a concentration of the total formulation in the washing solution of 0.2% at pH 10.0. (The pH of the washing solutions was adjusted, where necessary, by the addition of sodium hydroxide thereto.).

The average detergency units (DU) of the formulations is the final reflectance of the washed cloth minus the initial reflectance of the soiled cloth (the average of two runs), the reflectance being measured with a Gardner Automatic Colour Difference Metre, Model AC—3. Except where otherwise indicated the same procedure was used throughout the Examples for measuring the detergent properties of the compositions.

The formulations of the Examples and their detergency test results are shown in Table I below.

TABLE I

Component	Formulation of Examples (%)	
	4	5
Dicarboxyl cellulose of Example 3	50	—
Sodium tripolyphosphate	—	50
Sodium silicate	10	10
Sodium alkyl benzene sulphonate	18	18
Water	to 100	to 100
Average Detergency Units (DU)	28.6	30.2

*"Dacron" is a Registered Trade Mark.

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Example 6.

17.2 g. of pure cellulose (Celufi, $H_2O=5.7\%$) was oxidised to dialdehyde cellulose using 17.1 g. of sodium metaperiodate in 300 ml water in accordance with procedure described by Mehlretter for making dialdehyde starch in Methods in Carbohydrate Chemistry, edited by R. L. Whistler, Vol. IV, page 316 (1964), Academic Press. The yield of dialdehyde cellulose was 14.6 g. ($H_2O=7.2\%$). It contained 80% dialdehyde units (dry basis) as determined by the Hofreiter, et al method in Anal. Chem. 27 1930 (1955) and 20% anhydroglucose units by difference.

13.30 g. of the above dialdehyde cellulose was oxidised to dicarboxyl cellulose using 170 ml of a solution containing 40 g. of sodium chlorite, 12.6 ml of glacial acetic acid and water in accordance with the procedure described in Example 3 for preparing dicarboxyl starch. The yield of dicarboxyl cellulose was 15.1 g. ($H_2O=0.63\%$). It contained 53% dicarboxyl units (dry basis) as determined by the ion-exchange method, 27% dialdehyde units and 20% anhydroglucose units by difference from the composition of the starting dialdehyde cellulose.

Examples 7 and 8.

The procedure of Examples 4 and 5 was repeated using the dicarboxyl cellulose of Examples 6 and for comparative purposes sodium tripolyphosphate, and the results are shown in Table II below.

TABLE II

Component	Formulation of Examples (%)	
	7	8
Dicarboxyl Cellulose of Example 6	50	—
Sodium tripolyphosphate	—	50
Sodium silicate	10	10
Sodium alkyl benzene sulphonate	18	18
Water	to 100	to 100
Average Detergency Units (DU)	30.1	29.1

Example 9.

30 g. of sodium metaperiodate was suspended in 750 ml of water and concentrated hydrochloric acid added until the pH of the resultant solution was 3.5. After all the metaperiodate had dissolved 20 g. of starch was added to the stirred solution. The reaction was allowed to proceed for 18 hours in a darkened vessel, the temperature being maintained below $20^{\circ}C$. After this period, the metaperiodate consumption was complete and the dialdehyde starch filtered off. Removal of iodate ion was effected by washing with cold water. The resultant dialdehyde starch was suspended in 875 ml of water to which was added 25 ml of glacial acetic acid. 75 g. of commercial sodium chlorite (80%) was then added slowly over a period of 5 minutes. After stirring at room temperature for 4 hours, the reaction mixture was purged with gaseous nitrogen to remove excess chlorine dioxide. The reaction mixture was neutralised to pH 8.5 with caustic soda and dialysed for 8 hours against distilled water. 20 g. of dicarboxyl starch was precipitated from the solution using acetone (1 litre) and was found to have a dicarboxyl content of 65%.

Example 10.

The detergency of the dicarboxyl starch of Example 9 was determined by the procedure described in Example 2, except that the concentration of sodium dodecyl benzene sulphonate was increased to 0.1%. The detergency was found to be 64% whilst detergency of the corresponding comparative solution using sodium tripolyphosphate as detergency builder was 67%.

The hygroscopicity of the dicarboxyl starch of Example 9 was found to be comparable with sodium tripolyphosphate and much better than sodium polyacrylate when tested by the procedure described in Example 2.

Example 11.

17.1 g. of Corn Starch ($H_2O=12.4\%$) was oxidised to dialdehyde starch with a solution of 11.88 g. of sodium metaperiodate dissolved in 792 ml of distilled water at $0^\circ C$. for 36 hours using the procedure of Sloan, Hofreiter et al, Ind. Eng. Chem. 48 1165 (1956). The yield of dialdehyde starch was 16.34 g. ($H_2O=6.95\%$). It contained 64% dialdehyde units (dry basis), as determined by the method of Hofreiter et al—Anal. Chem. 27 1930 (1955) and 36% anhydroglucose units by difference.

13.95 g. of the above dialdehyde starch was oxidised to dicarboxyl starch in accordance with the procedure described in Example 3 except that the quantities of oxidising solution were 65 ml containing 34.2 g. of sodium chlorite, 11 ml of glacial acetic acid and water. The reaction time was $5\frac{1}{2}$ hours. The yield of dicarboxyl starch was 17.5 g. ($H_2O=0.30\%$). It contained 61% dicarboxyl units (dry basis), as determined by the ion-exchange method, 3% dialdehyde units and 36% anhydroglucose units by difference from the composition of the starting dialdehyde starch.

Examples 12 and 13.

Two detergent compositions were prepared using in one case the dicarboxyl starch of Example 11 and in the other case for comparison sodium tripolyphosphate as detergency builder. The formulations and detergency results are shown in Table III below.

TABLE III

Component	Formulation of Examples (%)	
	12	13
Dicarboxyl starch of Example 11	50	—
Sodium tripolyphosphate	—	50
Sodium silicate	10	10
Sodium alkyl benzene sulphonate	18	18
Water	to 100	to 100
Average Detergency Units (DU)	29.8	30.0

Example 14.

To a slurry of 30 g. of commercial dialdehyde starch ($H_2O=11.37\%$) containing 99.6% dialdehyde units (dry basis), as determined by the method of Hofreiter et al, Anal.Chem. 27 1930 (1955), in 200 ml of water at room temperature, was added a solution of 120 g. of sodium chlorite in a mixture of 200 ml of water and 40 ml of glacial acetic acid. The reaction mixture was stirred for three hours after which nitrogen was bubbled through the mixture to remove chlorine dioxide. After adjusting the pH to 8.3 with a sodium hydroxide solution, 600 ml of ethanol was added to precipitate the oxidised starch which came out as a gummy material. The product was redispersed in 100 ml of water and reprecipitated with 300 ml of ethanol. This purification procedure was repeated three more times in order to completely remove inorganic salts. After drying the product in a vacuum oven, the yield of dicarboxyl starch was 32.4 g. ($H_2O=4.44\%$). It contained 77% dicarboxyl units in sodium salt form, dry basis as determined by the ion-exchange method described by Hofreiter et al (JACS 79 6457 (1957)) and, 23% of dialdehyde units (dry basis) by difference from the composition of the starting dialdehyde starch.

Examples 15 to 24.

A series of detergent compositions were prepared by blending together the recited components including the dicarboxyl starch of Example 14. For comparative purposes detergent compositions were also prepared with sodium tripolyphosphate as the detergency builder. The compositions were then tested for detergency using the procedure of Examples 4 and 5. The formulations of the compositions and the detergency test results are given in Table IV below.

TABLE IV

Component	Formulation of Examples (%)									
	15	16	17	18	19	20	21	22	23	24
Dicarboxyl starch of Example 14	50	—	50	—	50	—	50	—	50	—
Sodium tripolyphosphate	—	50	—	50	—	50	—	50	—	50
Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 2.4:1$) ¹	10	10	10	10	10	10	10	10	10	10
Sodium alkyl benzene sulphonate ²	18	18	—	—	—	—	—	—	—	—
Neodol 45—11 ³	—	—	10	10	—	—	—	—	—	—
Sodium N-(2-hydroxy C_{14-18} alkyl)-N-methyl taurate	—	—	—	—	18	18	—	—	—	—
Sulphobetaine DCH ⁴	—	—	—	—	—	—	18	18	—	—
Sodium C_{15-18} α -olefin sulphonate	—	—	—	—	—	—	—	—	18	18
Water	← to 100% →									
Average Detergency Units (DU)	28.2	28.2	28.4	26.9	27.3	27.7	28.4	27.9	28.4	28.4

¹Except where otherwise indicated this type of sodium silicate was used throughout the Examples.

²Sodium linear secondary alkyl ($\text{C}_{10}-\text{C}_{18}$) benzene sulphonate. Except where otherwise indicated this type of alkyl benzene sulphonate was used throughout the Examples.

³Nonionic detergent active compound made by reacting a modified Oxo-type $\text{C}_{14}-\text{C}_{15}$ alcohol with an average of 11 moles of ethylene oxide.

⁴Coco-dimethylsulphopropylbetaine.

Example 25.

30 g of commercial dialdehyde starch ($H_2O=11.4\%$) containing 91% dialdehyde units (dry basis) as determined by the method of Hofreiter et al—Anal. Chem. 27 1930 (1955) and 9.0% anhydroglucose units by difference was slurried in 200 ml of water at room temperature. During vigorous stirring, a solution of 52 g. of sodium chlorite in 83 ml of water was then added followed by the slow addition (to prevent foaming) of 17 ml of glacial acetic acid. The reaction mixture was stirred at room temperature for an additional 3 hours. After bubbling nitrogen through the mixture to remove chlorine dioxide, 600 ml of ethanol was added to precipitate the dicarboxyl starch. The white paste obtained was redispersed in 30 ml water and reprecipitated with ethanol. This purification procedure was repeated three more times to remove inorganic salts. The product was dried in a vacuum oven to give 24.5 g. of oxidised dicarboxyl starch ($H_2O=12.13\%$). It contained 56% of dicarboxyl units (dry basis) as determined by the ion-exchange method and 35% dialdehyde units and 9% of anhydroglucose units by difference from the composition of the original dialdehyde starch.

Example 26.

The procedure described in Example 25 was repeated except that a solution of 86 g of sodium chlorite in 140 ml of water and 29 g. of glacial acetic acid was used in place of the previous quantities stated. The yield of dicarboxyl starch was 32.0 g. ($H_2O=10.24\%$). It contained 87% of dicarboxyl units (dry basis), as determined by the ion-exchange method, 4% of dialdehyde units and 9% of anhydroglucose units (dry basis) by difference from the composition of the original dialdehyde starch.

Example 27.

The procedure described in Example 25 was repeated except that a solution of 17.1 g. of sodium chlorite in 46 ml of water and 5.7 ml of glacial acetic acid was used in place of the previous quantities stated in Example 25. The yield of dicarboxyl starch was 27.1 g. ($H_2O=7.07\%$). It contained 19% of dicarboxyl units (dry basis), as determined by the ion exchange method, 72% of dialdehyde units and 9% of anhydroglucose units by difference from the composition of the original dialdehyde starch.

Examples 28 to 31.

Detergent compositions were made using the dicarboxyl starches of Examples 25, 26 and 27 and for comparative purposes, sodium tripolyphosphate, as the detergency builder. The detergency of the compositions was determined by the procedure described in Examples 4 and 5 and the results are shown in Table V below:—

TABLE V

Component	Formulation of Examples (%)			
	28	29	30	31
Dicarboxyl starch of Example 25	50	—	—	—
Dicarboxyl starch of Example 26	—	50	—	—
Dicarboxyl starch of Example 27	—	—	50	—
Sodium tripolyphosphate	—	—	—	50
Sodium silicate	10	10	10	10
Sodium alkyl benzene sulphonate	18	18	18	18
Water	← to 100% →			
Average Detergency Units (DU)	27.2	29.2	22.5	29.4

Example 32.
19.75 g. of commercial dialdehyde starch ($H_2O=11.37\%$) containing 99.6% dialdehyde units (dry basis) is determined by the method of Hofreiter et al—Anal. Chem. 27 1930 (1955), was oxidised to the dicarboxyl starch by the method described in Example 3, using 150 ml of a freshly made solution containing 88.8 g. of sodium chlorite, 28 ml of glacial acetic acid and water. The yield was 21.1 g. of dicarboxyl starch ($H_2O=1.01\%$) containing 92% of dicarboxyl units (dry basis) as determined by the ion-exchange method and 8% of dialdehyde units by difference from the composition of the original dialdehyde starch.

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Examples 33 to 40.

A series of detergent compositions were prepared using the dicarboxyl starch of Example 32, or for comparative purposes, sodium tripolyphosphate, as a detergent builder at different concentrations in the compositions. The formulations of the compositions and their detergencies are shown in Table VI below.

TABLE VI

Component	Formulation of Examples (%)									
	33	34	35	36	37	38	39	40		
Dicarboxyl starch of Example 32	70	—	50	—	30	—	10	—		
Sodium tripolyphosphate	—	70	—	50	—	30	—	10		
Sodium silicate	10	10	10	10	10	10	10	10		
Sodium alkyl benzene sulphonate	18	18	18	18	18	18	18	18		
Water	← to 100% →									
Average Detergency Units (DU)	31.1	30.0	29.6	29.5	29.3	28.7	18.5	19.8		

Examples 41 and 42.

Two detergent compositions were made using in one case the dicarboxyl starch of Example 32 and in the other case for comparison, sodium tripolyphosphate as detergency builder. The detergency units of the compositions were then determined using water of different degrees of hardness, and the results are shown in Table VII below.

TABLE VII

Component	Formulation of Examples (%)	
	41	42
Dicarboxyl starch of Example 32	50	—
Sodium tripolyphosphate	—	50
Sodium silicate	10	10
Sodium alkyl benzene sulphonate	18	18
Water	to 100	to 100

Water Hardness PPM	Average Detergency Units (DU)	
90	31.8	31.1
180	29.6	29.5
270	29.6	28.9
360	27.2	26.3

Example 43.

The procedure of Example 14 was repeated except that the quantities were 10 g. of the commercial dialdehyde starch, 40 g. of sodium chlorite in 70 ml of water and 12.6 ml of glacial acetic acid. No pH adjustment was made after the reaction. The yield of dicarboxyl starch was 10.5 g. ($H_2O=12.85\%$). It contained 52% dicarboxyl units (dry basis) as determined by the ion-exchange method and by difference 48% dialdehyde units.

Examples 44 and 45.

Two detergent compositions were made up using in one case the dicarboxyl starch of Example 43 and in the other case for comparison sodium tripolyphosphate as the detergency builder. The detergencies of the compositions were measured at different product concentrations in the wash liquor and the results are shown in Table VIII below.

TABLE VIII

Component	Formulation of Examples (%)	
	44	45
Dicarboxyl starch of Example 43	50	—
Sodium tripolyphosphate	—	50
Sodium silicate	10	10
Sodium alkyl benzene sulphonate	18	18
Water	to 100	to 100
Use Formulation Concentration (%)	Average Detergency Units	
0.20	24.0	23.8
0.15	22.7	22.1
0.10	17.0	16.0
0.05	6.1	6.3

Examples 46 to 49.
 Detergent compositions were prepared using the dicarboxyl starch of Example 43 in combination with sodium nitrilotriacetate (NTA) as mixed detergency builders, and for comparative purposes a composition was made with sodium nitrilotriacetate as the sole builder. The formulations of the Examples and their detergencies are shown in Table IX below.

TABLE IX

Component	Formulation of Examples (%)			
	46	47	48	49
Dicarboxyl starch of Example 43	37.5	25	12.5	—
NTA	12.5	25	37.5	50
Sodium silicate	10	10	10	10
Sodium alkyl benzene sulphonate	18	18	18	18
Water	← to 100% →			
Average Detergency Units (DU)	26.0	25.0	26.3	22.9

Example 50.

30 g. of commercial dialdehyde starch ($H_2O=11.37\%$) containing 99.6% dialdehyde units (dry basis), as determined by the method of Hofreiter et al—Anal. Chem. 27 1930 (1955), was oxidised according to the procedure described in Example 25 except that 120 g. of sodium chlorite dissolved in 200 ml water and 3.78 ml of acetic acid was used instead of the previously stated quantities. The yield of dicarboxyl starch was 32.6 g. ($H_2O=7.3\%$). It contained 70% of dicarboxyl units as determined by the ion-exchange method and 30% of dialdehyde units by difference from the composition of the starting dialdehyde starch.

Examples 51 to 54.

Detergent compositions were prepared using mixtures of the dicarboxyl starch of Example 50 and sodium tripolyphosphate as detergency builder, and in another comparative example sodium tripolyphosphate was the sole detergency builder. The formulations of the Examples and the detergent properties are shown in Table X below:

TABLE X

Component	Formulation of Examples (%)			
	51	52	53	54
Dicarboxyl starch of Example 50	37.5	25.0	12.5	—
Sodium tripolyphosphate	12.5	25.0	37.5	50
Sodium silicate	10	10	10	10
Sodium alkyl benzene sulphonate	18	18	18	18
Water	← to 100% →			
Average Detergency Units (DU)	23.7	24.9	24.3	24.4

Example 55.

The procedure and quantities of Example 32 were repeated except that the reaction mixture was stirred at room temperature for only 3 hours instead of 24 hours. The yield of dicarboxyl starch was 26.9 g. ($H_2O=0.31\%$). The product contained 91% of dicarboxyl units (dry basis) as determined by the ion-exchange method and 9% of dialdehyde units by difference from the composition of the starting dialdehyde starch.

Examples 56 and 57.

A detergent composition was prepared using the dicarboxyl starch of Example 55 and for comparative purposes another composition was made with sodium tripolyphosphate as detergency builder. The detergent properties were determined under the conditions described for Examples 4 and 5 except that a solution of pH7 was used (the pH being adjusted with sulphuric acid). The test results are shown in Table XI below:

TABLE XI

Component	Formulation of Examples (%)	
	56	57
Dicarboxyl starch of Example 55	50	—
Sodium tripolyphosphate	—	50
Sodium alkyl benzene sulphonate	18	18
Water	to 100	to 100
Average Detergency Units (DU)	29.4	29.2

Examples 58 to 63.

5 642 g. of sodium metaperiodate was suspended in 12 l. of water and concentrated hydrochloric acid was added until the pH of the resultant solution was 3.5. After all the metaperiodate had dissolved 486 g. of starch was added to the stirred solution. The reaction was allowed to proceed for 72 hours in a darkened vessel under gaseous nitrogen, the temperature being maintained at 20° C. After this period the metaperiodate consumption was complete and the dialdehyde starch filtered off. Removal of iodate ion was effected by washing with cold water and the product dried under vacuo. Analysis of the dialdehyde content by the method of Hofreiter et al. Anal. Chem., 27, 1930 (1955) indicated the presence of 94.4% dialdehyde units. 50 g of dialdehyde starch was slurried in 1 l. of water together with 0.1 g. of sodium carbonate for a period of 30 minutes. 310 g. of commercial sodium chlorite (80%) was added followed by 80 ml of glacial acetic acid added slowly over a period of 10 minutes. After 24 hours, the solution was purged with gaseous nitrogen to expel chlorine dioxide and the pH of the solution adjusted to 8.3, and the product precipitated from 2.5 l. of industrial spirit. The dicarboxyl starch was redissolved in the minimum concentration of water (about 100 ml.) and reprecipitated with 300 ml of industrial spirit. This procedure was repeated twice after which the product was chloride ion free. Yield 47.6 g. The product contained 86.3% dicarboxyl units and by difference 8.1% dialdehyde units and 5.6% anhydroglucose units.

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15 The oxidation of the dialdehyde starch was repeated under different conditions to give dicarboxyl starches of different dicarboxyl contents as shown in Table XII below, which includes the figures given above:

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TABLE XII

Example	NaClO ₂ (g)	CH ₃ COOH (ml)	Yield (g)	Analysis		
				Dicarboxyl units	Dialdehyde units	Anhydro- glucose units
58	310	80.0	47.6	86.3	8.1	5.6
59	164	42.8	47.6	75.1	19.3	5.6
60	115	30.6	48.9	73.0	21.4	5.6
61	110	28.5	47.5	65.3	29.1	5.6
62	62	16.4	48.5	60.7	34.4	5.6
63	40	10.6	49.1	54.0	40.4	5.6

Examples 64 and 65.

The procedure described for making the dialdehyde starch for Examples 58 to 63 was repeated to make a dialdehyde starch of lower dialdehyde unit content, using 321 g of sodium metaperiodate and a reaction time of 24 hours. The product contained 64.5% of dialdehyde units and 35.5% of anhydroglucose units.

This dialdehyde starch was oxidised using the procedure described for Examples 58 to 63, the amounts of the reactants and the analysis of the products being as shown in Table XIII below:

TABLE XIII

Example	NaClO ₂ (g)	CH ₃ COOH (g)	Yield (g)	Analysis		
				Dicarboxyl units	Dialdehyde units	Anhydro- glucose units
64	52	39.3	47.2	64.5	0	35.5
65	62	25	48.0	47.0	17.5	35.5

Examples 66 to 75.

The detergency building capacities of the dicarboxyl starches made in Examples 58 to 65 were determined by the procedure described in Example 2. The simulated product compositions used at a concentration of 0.2% and their detergencies determined by the radio-tracer method described in Example 2 are shown in Table XIV below, which includes for comparative purposes similar results for a composition built with sodium tripolyphosphate and an unbuilt composition:

TABLE XIV
Formulation of Examples (%)

Component	66	67	68	69	70	71	72	73	74	75
Dicarboxyl starch of Example 58	50	—	—	—	—	—	—	—	—	—
Dicarboxyl starch of Example 59	—	50	—	—	—	—	—	—	—	—
Dicarboxyl starch of Example 60	—	—	50	—	—	—	—	—	—	—
Dicarboxyl starch of Example 61	—	—	—	50	—	—	—	—	—	—
Dicarboxyl starch of Example 62	—	—	—	—	50	—	—	—	—	—
Dicarboxyl starch of Example 63	—	—	—	—	—	50	—	—	—	—
Dicarboxyl starch of Example 64	—	—	—	—	—	—	50	—	—	—
Dicarboxyl starch of Example 65	—	—	—	—	—	—	—	50	—	—
Sodium tripolyphosphate	—	—	—	—	—	—	—	—	50	—
Sodium dodecyl benzene sulphonate	25	25	25	25	25	25	25	25	25	25
Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 2/1$)	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
Water	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100
% Detergency	70.1	74.4	73.0	70.9	45.2	36.5	29.9	40.2	71.7	5.0

Example 76.

To a solution of 60 g. of sodium metaperiodate in 1,250 ml of water which had been adjusted to pH 3.5 by the addition of 1 ml of concentrated hydrochloric acid, was added 40 g. of alginic acid. The solution was stirred in a darkened vessel at room temperature for 7 days. After this period 75% of the sodium metaperiodate had been consumed. The dialdehyde derivative was filtered off and washed with cold water in order to remove sodium iodate and unreacted sodium metaperiodate.

Oxidation to the dicarboxyl derivative of alginic acid was effected using 72 g. of commercial sodium chlorite (80%) in 650 ml of water containing 22.4 ml of glacial acetic acid. After stirring for a period of 2 hours, the dicarboxyl alginic acid was precipitated using 5 l of acetone after excess chlorine dioxide had been expelled using gaseous nitrogen. The product was dissolved in water and the pH of the solution adjusted to pH 8.5, and then dialysed against distilled water for 8 hours after which 38 g. of the dicarboxyl derivative (containing about 75% of dicarboxyl units) was precipitated using 2 l. of acetone.

Example 77.

The detergency of the dicarboxyl alginate prepared in Example 76 was determined by the procedure described in Example 2 and found to be 67.4%, that is well above the corresponding figure of 61.7% for a detergent composition in which the dicarboxyl alginate was replaced by an equal weight of sodium tripolyphosphate. By way of comparison, the detergency of a further solution in which the dicarboxyl alginate was replaced by unoxidised sodium alginate was only 34.6%.

The hygroscopicity of the dicarboxyl alginate of Example 76 was found to be comparable with sodium tripolyphosphate and much better than sodium polyacrylate when tested by the procedure described in Example 2.

Example 78.

Monocarboxyl corn starch, 19.4 g. (9.4% water; 75% monocarboxyl units-dry basis), prepared according to Example 1 of US patent No. 2,472,590 was converted into monocarboxyl dialdehyde corn starch using the method described by Mehlretter ("Methods in Carbohydrate Chemistry" IV, p. 316, Academic Press, 1964) for the conversion of corn starch into dialdehyde starch. Yield of monocarboxyl dialdehyde corn starch: 14.0 g. (0.8% water).

Monocarboxyl dialdehyde corn starch, 12.0 g. (0.8% H₂O; 0.074 mole) from above was dissolved in 340 ml of water containing 0.0342 g. of Na₂CO₃ at 88° C. with stirring. After cooling to room temperature, there was added 90 ml of an aqueous solution containing 48.4 g. (0.59 mole) of sodium chlorite and 15.3 ml of glacial acetic acid and the reaction mixture stirred for 5½ hours. Nitrogen was then bubbled through the solution to remove chlorine dioxide. The reaction mixture was then poured into 2 volumes of industrial alcohol to precipitate the tricarboxyl starch. The gummy white product was redissolved in a minimum amount of water, and reprecipitated with industrial alcohol. A test for Cl⁻ in the product was then negative. The product was dried in a vacuum oven over P₂O₅ to give 13.3 g. of tricarboxyl starch (% water=1.2). Analysis by ion exchange and titration with standard alkali indicated an apparent tricarboxyl unit content of approximately 77% (uncorrected for monocarboxyl and dicarboxyl species which may be present to a small extent) and the balance, 22% anhydroglucose units by difference.

Example 79.

30.1 g. (11.6% H₂O) of commercial sodium alginate (Kelset) was added slowly to 1400 ml of water at 88° C. As the mixture became thick powdered sodium chloride was added to thin it out. A total of 20 g. of NaCl was thus added. The resulting homogeneous mixture was cooled to 55° C. and a solution of 42 g of sodium periodate in 300 ml of water was then added gradually over a 45 minute period with stirring. After stirring the mixture for an additional 24 hours, 2 litres of industrial alcohol was added to precipitate the product. The product was filtered and purified by dissolving in a minimum amount of water and reprecipitating by the addition of two volumes of industrial alcohol. After repeating the purification procedure five times, the product was dried in vacuo over P₂O₅ to give 34 g. of dialdehyde sodium alginate (7.3% H₂O).

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30 g. of the above prepared dialdehyde sodium alginate was dispersed in 850 ml of hot water (88° C.) containing 0.085 g. of sodium carbonate while stirring vigorously. After cooling the mixture to room temperature, 180 ml of an aqueous solution containing 99.05 g. of NaClO₂ and 32 ml of acetic acid was added slowly. The reaction mixture was then stirred for 5½ hours. Nitrogen was next bubbled through the solution to remove chlorine dioxide. The reaction mixture was then poured into two volumes of industrial alcohol, while stirring vigorously, to precipitate the product. After decanting the supernatant liquor, the product was treated with water to form a paste and then reprecipitated with industrial alcohol. The product, which showed a negative test for Cl⁻ was dried in a vacuum oven over P₂O₅ to give 30.6 g. of dicarboxyl alginate (2.9% H₂O). Analysis of a sample by ion-exchange and titration with standard alkali indicated a tricarboxyl unit content of 69% (dry basis) and the balance, 31% anhydro-D-mannuronate groups by difference.

Example 80.

40 g. (<10% H₂O) of dialdehyde sodium alginate was prepared according to the procedure described in Example 79.

Dialdehyde sodium alginate, (8.5 g.) was dissolved in 125 ml of water and filtered under pressure through an ultrafiltration membrane (reverse osmosis) to separate inorganics. The concentrated product was repeatedly diluted with water and subjected to reverse osmosis until the filtrate gave only a slight test for iodate ion. The purified product was then dried in a vacuum oven over P₂O₅ to give 7.1 g. of purified dialdehyde sodium alginate.

Dialdehyde sodium alginate, (15 g.) prepared as described above was oxidised with sodium chlorite according to the procedure described in Example 79 to yield 10.0 g. (0.6% H₂O) of dicarboxyl alginate. Analysis of a sample by ion-exchange and titration with standard alkali indicated a tricarboxyl unit content of 85% and the balance, 15% anhydro-D-mannuronate groups by difference.

Examples 81 to 84.

Four detergent compositions were prepared using the tricarboxyl starch of Example 78, the dicarboxyl alginates of Example 79 and 80 and for comparative purposes sodium tripolyphosphate as detergency builder. The detergencies of the compositions were then determined and the results are shown in Table XV below.

TABLE XV

Component	Formulation of Examples (%)			
	81	82	83	84
Tricarboxyl starch of Example 78	50	—	—	—
Dicarboxyl alginate of Example 79	—	50	—	—
Dicarboxyl alginate of Example 80	—	—	50	—
Sodium tripolyphosphate	—	—	—	50
Sodium silicate	10	10	10	10
Sodium alkyl benzene sulphonate	18	18	18	18
Water	← to 100 →			
Average Detergency Units (DU)	29.3	26.6	27.5	27.6

Example 85.

5 Corn starch, 18.5 g. (12.4% H_2O), was suspended in 200 ml water. Then 1135 g. of 5.25% sodium hypochlorite solution was added while stirring. The pH was adjusted to 9 and maintained at 9 with the addition of 50% sodium hydroxide solution as required. A clear solution was obtained in about 2 hours. The reaction mixture was stirred for a total of 70 hours and then concentrated in vacuo to 300 c.c. The filtrate was then added to 1500 ml of ethanol and the resulting precipitate filtered. The product was purified by dissolving in about 100 ml of water and reprecipitating with about 1 litre of alcohol until a negative Cl^- test was obtained. (A total of four reprecipitations was required). The yield of dicarboxyl starch was 18.5 g. (2.4% H_2O). It contained 78% dicarboxyl units (dry basis), as determined by ion exchange and titration of a sample with standard sodium hydroxide, and 32% anhydroglucose units by difference from the starting composition.

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Example 86.

15 Corn starch, 18.5 g. (11.9% H_2O) was added to 895 g. of 5.25% sodium hypochlorite solution with stirring. The pH was maintained at 9 by the addition of 50% sodium hydroxide solution as required. The temperature rose as high as 41° C. A clear solution was obtained after about one hour of reaction. The reaction mixture was allowed to stand (with stirring) for a total of 24 1/2 hours. The reaction mixture was then added to sufficient ethanol to form an 80% ethanolic solution.

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25 The dicarboxyl starch product which precipitated was isolated by decantation of the supernatant solution and purified by dissolving in 200 ml of water and reprecipitating with 1400 ml ethanol. The purification step was repeated using 100 ml of water and 500 ml of ethanol. The solution was decanted leaving a viscous material which was dried in vacuo. The yield of dicarboxyl starch product was 20.8 g. (2.5% H_2O) containing 69% dicarboxyl units (dry basis), as determined by ion-exchange and titration of a sample with standard sodium hydroxide, and 31% anhydroglucose units by difference from the starting composition.

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Examples 87 to 100.

30 A series of detergent compositions were prepared using the dicarboxyl starches of Examples 85 or 86 or for comparison sodium tripolyphosphate as detergency builder. The formulation of the Examples and their detergencies are shown in Table XVI below.

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TABLE XVI

Component	Formulation of Examples (%)													
	87	88	89	90	91	92	93	94	95	96	97	98	99	100
Dicarboxyl starch of Example 85	50	—	25	—	—	—	—	—	50	—	50	—	50	—
Dicarboxyl starch of Example 86	—	—	—	—	50	—	50	—	—	—	—	—	—	—
Sodium tripolyphosphate	—	50	—	25	—	50	—	50	—	50	—	50	—	50
Sodium silicate solids	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Sodium alkyl benzene sulphonate	18	18	18	18	18	18	—	—	—	—	—	—	—	—
Neodol 45—11	—	—	—	—	—	—	10	10	—	—	—	—	—	—
Sodium N-(2-hydroxy C ₁₄₋₁₈ alkyl)-N-methyl taurate	—	—	—	—	—	—	—	—	18	18	—	—	—	—
Sulphobetaine DCH	—	—	—	—	—	—	—	—	—	—	18	18	—	—
Sodium C ₁₅₋₁₈ α -olefin sulphonate	—	—	—	—	—	—	—	—	—	—	—	—	18	18
Water	to 100													
Average Detergency Units (DU)	27.5	28.5	26.6	27.1	29.0	30.3	24.8	28.2	23.8	27.1	25.4	27.7	26.7	28.9

Examples 101 to 106.

A series of detergent compositions were prepared with different amounts of the dicarboxyl starch of Example 86 or for comparison, sodium tripolyphosphate as detergency builder. The formulations of the Examples and their detergent properties are shown in Table XVII below.

TABLE XVII

Formulation of Example (%)

Component	101	102	103	104	105	106
Dicarboxyl starch of Example 86	70	—	50	—	10	—
Sodium tripolyphosphate	—	70	—	50	—	10
Sodium silicate	10	10	10	10	10	10
Sodium alkyl benzene sulphonate	18	18	18	18	18	18
Water	← to 100 →					
Average Detergency Units (DU)	29.8	30.4	29.5	30.5	26.9	28.1

Example 107.

Corn starch (0.1 mole; 18.1 g. or 88.9% solids) was dispersed in a minimum quantity of distilled water (~30—40 ml) containing NaHCO_3 (0.01 mole) in a container protected from light. 8.6% NaOCl solution (0.3 mole) was added to the stirred starch suspension in portions. The reaction mixture was stirred and maintained at a pH between 8—9 with 50% NaOH solution and the temperature at 20—30° C. The addition period and subsequent reaction time totalled 4.8 hours. NaHSO_3 was then added to the clear solution until a negative test was obtained with KI-starch paper. An equal volume of ethanol was added with vigorous stirring which was continued for a short time. The lower layer was then separated from the solution and the product was reprecipitated from 150 ml distilled water with an equal volume of ethanol until a negative Cl^- test resulted. The product was dried under vacuum. The yield was 95% of material having 38.4% COONa , corresponding to a 67% dicarboxyl starch content.

Examples 108 to 123.

A series of detergent compositions were made incorporating the dicarboxyl starch of Example 107 with various amounts of different detergent active compounds, and comparative compositions were made with sodium tripolyphosphate as the detergency builder. The detergent properties of the Examples were determined by the procedure described for Examples 4 and 5 except that the product concentrations in the washing liquor was decreased to 0.1%. The formulations of the Examples and their detergencies are shown in Table XVIII below.

TABLE XVIII

Component	Formulation of Examples (%)															
	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123
Dicarboxyl starch of Example 107	50	50	50	—	50	50	50	—	50	50	50	—	50	50	50	—
Sodium tripolyphosphate	—	—	—	50	—	—	—	50	—	—	—	50	—	—	—	50
Sodium C ₁₅₋₁₈ α -olefin sulphonate	18	27	36	18	—	—	—	—	—	—	—	—	—	—	—	—
Sodium-N-(2-hydroxy C ₁₄ -C ₁₈ alkyl)-N-methyl taurate	—	—	—	—	18	27	36	18	—	—	—	—	—	—	—	—
Sulphobetaine DCH	—	—	—	—	—	—	—	—	18	27	36	18	—	—	—	—
Sodium alkyl benzene sulphonate	—	—	—	—	—	—	—	—	—	—	—	—	18	27	36	18
Sodium silicate	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Water	to 100															
Average Detergency DU's	17.2	19.1	21.9	17.7	18.1	19.8	20.6	17.5	18.4	20.8	21.2	21.9	20.1	22.7	23.4	23.7

Examples 124 to 127.

5 A series of dicarboxyl starches were made under different conditions of pH, but
 using in all cases the same amount of sodium hypochlorite (4 moles of NaOCl to 1
 mole of anhydroglucose units), by the following procedure: 18.0 g. of corn starch
 (90% solids) was added to a solution of sodium hypochlorite diluted with ion-free
 water maintained at pH 9.5. The reaction flask was darkened to exclude light, and the
 solution maintained at 18° C. On addition of the starch the pH of the reaction mixture
 began to fall. When the pH of the solution reached the desired value it was maintained
 by addition of caustic soda (50%). Initially the caustic soda consumption was rapid
 (about 10 ml) and external cooling was required in order to maintain the temperature
 within the range 22—25° C. After 24 hours, the sodium hypochlorite had been com-
 pletely consumed. The pH of the reaction mixture was adjusted to pH 9.0 by addition
 of caustic soda solution. The product was precipitated by addition of 700 ml of
 absolute alcohol and filtered off. It was redissolved in 100 ml of water and reprecipitated
 with 250 ml of absolute alcohol. This washing procedure was repeated a further two
 times. The product was now chloride ion free. The apparent dicarboxyl unit content of
 the product was determined by ion exchange and titration of a sample with standard
 sodium hydroxide.
 20 The detergency of the resultant dicarboxyl starches were determined using the
 procedure of Example 2. The variable conditions in the reaction and the detergencies
 of the products are shown in Table XIX below.

TABLE XIX

Example	pH	% conc. of NaOCl soln.	NaOCl soln. (g)	Water (g)	Dicarboxyl unit Content	Detergency %
124	7.75	19.9	234	26	72.6	57.0
125	8.0	14.4	206	54	84.0	62.9
126	8.25	14.5	205	55	80.6	67.8
127	8.5	13.1	228	32	75.0	54.2

A comparative test using sodium tripolyphosphate as the detergency builder
 gave a detergency of 71.5%.

Examples 128 to 130.

25 For comparative purposes, the dicarboxyl starches of Examples 125 and 126 and
 sodium tripolyphosphate were also tested for detergency building properties using the
 light reflectance method described in Examples 4 and 5. The formulations of the
 products and the test results are shown in Table XX below.

TABLE XX

Component	Formulation of Examples (%)		
	128	129	130
Dicarboxyl starch of Example 125	50	—	—
Dicarboxyl starch of Example 126	—	50	—
Sodium tripolyphosphate	—	—	50
Sodium silicate	10	10	10
Sodium alkyl benzene sulphonate	18	18	18
Water	← to 100 →		
Average detergency units (DU)	26.0	26.9	26.7

Examples 131 and 132

Two dicarboxyl starches were prepared by the procedure described for Examples 124 to 127, except that the concentration and mole ratios of sodium hypochlorite solution were increased. The variable conditions of the reaction and the detergencies of the products as determined by the method of Example 2 are shown in Table XXI below:

TABLE XXI.

Example	pH	% con. of NaOCl	NaOCl solution (g)	Dicarboxyl unit content	Detergency %
131	8.25	12.9	295	82.9	68
132	8.25	15.0	300	83.5	72

For comparative purposes the detergency (%) of composition using sodium tripolyphosphate was determined and found to be 70.1%.

Example 133.

107 g. of sodium meta periodate was added to 2,500 ml. of water and the pH of the resultant solution adjusted to pH 3.5 by the addition of concentrated hydrochloric acid. 110 g. of sodium carboxymethylcellulose (degree of substitution=0.6) was added to the solution which was stirred for a period of 7 days in a darkened vessel under a nitrogen atmosphere, at 5—15° C. After this period 70.3% of the sodium meta periodate had been consumed and the dialdehyde carboxymethylcellulose was dialysed against ion-free water to remove sodium iodate and sodium meta periodate. The solution was poured into 2,500 ml of acetone and the precipitated dialdehyde carboxymethylcellulose was collected by filtration.

12 gms. of the dialdehyde carboxymethylcellulose were further oxidised using 31 g. of commercial sodium chlorite (80%) and 10 ml. of glacial acetic acid in 35 ml. of water. After a period of 4 hours the reaction mixture was purged with gaseous nitrogen to remove excess chlorine dioxide. The product was neutralised to pH.5 using 50% NaOH, and sodium chloride was removed by successive reprecipitation with 300 ml. of alcohol from a solution in 50 ml. of water. 11.2 g. of the dicarboxyl sodium carboxymethylcellulose was recovered, and was found to contain 67.5% dicarboxyl units.

Example 134.

16.5 g. of sodium meta periodate were added to 475 ml. of water and the pH of the resultant solution adjusted to pH 3.5 with concentrated hydrochloric acid. 15 g. of ethyl cellulose (degree of substitution=0.5) was added to the solution which was stirred for a period of 7 days in a darkened vessel under a nitrogen atmosphere as 5—15° C. After this period 83.5% of the sodium meta periodate had been consumed and the dialdehyde ethylcellulose was dialysed against ion-free water to remove sodium iodate and sodium meta periodate. The solution was poured into 500 ml. of acetone and the precipitated dialdehyde/ethylcellulose was collected by filtration.

The dialdehyde/ethylcellulose was further oxidised using 19 g. of commercial sodium chlorite (80%), and 6.3 ml. of glacial acetic acid in 80 ml. of water. After a period of 4 hours the reaction mixture was purged with gaseous nitrogen to remove excess chlorine dioxide. The product was neutralised to pH 8.5 using 50% NaOH and sodium chloride was removed by successive reprecipitations with 250 ml. of alcohol from a solution in 25 ml. of water. 14.2 g. of dicarboxyl ethylcellulose was recovered, and was found to contain 64.2% dicarboxyl units.

The detergency building properties of the dicarboxyl sodium carboxymethylcellulose of Example 133 and the dicarboxyl ethylcellulose of Example 134 were determined by the procedure described in Example 2. The detergencies (%) of the compositions using these materials were, respectively, 46% and 32%, whilst the detergency (%) of a control composition with sodium tripolyphosphate as the detergency builder was 72%. A further control composition without a detergency builder had a detergency of only 5.2%.

Examples 135 to 138.

In order to compare the detergent properties of dicarboxyl starches with a monocarboxyl starch in which the primary hydroxyl group had been oxidised to a carboxyl group, a starch was oxidised to monocarboxyl starch by the process of Example 1 of US patent No. 2,472,590. A detergent composition was then prepared from this monocarboxyl starch, and tested for detergency with other compositions incorporating the dicarboxyl starches of Examples 32 and 86 and sodium tripolyphosphate as detergency builder. The results are shown in Table XXII below.

TABLE XXII

Component	Formulation of Examples %			
	135	136	137	138
Monocarboxyl starch (20.7% COOH content)	50	—	—	—
Dicarboxyl starch of Example 32	—	50	—	—
Dicarboxyl starch of Example 86	—	—	50	—
Sodium tripolyphosphate	—	—	—	50
Sodium silicate	10	10	10	10
Sodium alkyl benzene sulphonate	18	18	18	18
Water	← to 100 →			
Average Detergency Units (DU)	20.3	27.7	27.9	28.1

These results show the dicarboxyl starches to be much superior to the monocarboxyl starch.

Attention is directed to the Applicants' copending patent application No. 40100 of 1970 (Serial No. 1,330,122).

WHAT WE CLAIM IS:—

- 5 1. A detergent composition comprising a detergent active compound and more than 5% up to 90% by weight of a water-soluble or dispersible oxidised polysaccharide containing at least about 20% (as herein defined) of dicarboxyl units, the ratio by weight of the detergent active compound to the oxidised polysaccharide being from 3:1 to 1:10. 5
2. A detergent composition according to claim 1, comprising from 20% to 60% by weight of the oxidised polysaccharide.
- 10 3. A detergent composition according to any of the preceding claims, wherein the oxidised polysaccharide is derived from starch or cellulose. 10
4. A detergent composition according to any of the preceding claims, wherein the oxidised polysaccharide contains at least 50% of dicarboxyl units.
- 15 5. A detergent composition according to any of the preceding claims, wherein a polysaccharide oxidised by sodium hypochlorite at a pH of from 7.5 to 9 is used. 15
6. A detergent composition according to claim 5, wherein the polysaccharide is oxidised by sodium hypochlorite at a pH of from 8 to 8.5.
7. A detergent composition according to claim 1, substantially as described herein with reference to any of Examples 2, 10 and 77.
- 20 8. A detergent composition according to claim 1 substantially as described herein with reference to any of Examples 58 to 75, 78 to 84 and 107 to 138. 20

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